Pressure- and temperature-induced M_3 phonon softening in ReO_3

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We have investigated the temperature and pressure variation of the M_3 phonon mode of ReO_3 by inelastic neutron scattering on a single crystal. The energy of the M_3 phonon mode decreases with decreasing temperature contrary to the normal hardening behavior. The energy of this mode also decreases with increasing pressure and tends to zero at about 3.5 kbar at $T=150$ K. The M_3 mode softening drives the pressure-induced phase transition in ReO_3. The temperature-induced softening of the M_3 mode on lowering the temperature can be understood from the known negative thermal-expansion behavior and also from the fact that the high-pressure phase can also be approached at ambient pressure by cooling. In order to understand the M_3 phonon softening in ReO_3 we have done lattice-dynamical calculations that support the qualitative arguments given above.

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I. INTRODUCTION

Transition-metal oxides have been the subject of renewed interest ever since high-temperature superconductivity was discovered in copper oxide materials. The transition-metal oxides with narrow d bands form strongly correlated Mott-Hubbard system for which the conventional band theory is no longer valid.[1] ReO_3 is one of the very few simple metallic oxides where the band theory alone can provide adequate account of their properties. ReO_3 seems to belong to the normal class of conventional-band Fermi liquids with electron-phonon interactions dominating the resistivity.[2] The conductivity of ReO_3 is comparable to that of Ag. ReO_3 crystallizes in the cubic space group ($Pm3m$) with the undistorted perovskitelike DO_9-type structure with lattice constant $a=3.74$ Å. The structure consists of corner-linked ReO_6 octahedra with Re at the centers and linear Re-O-Re links. Among the numerous perovskitelike compounds ReO_3 belongs to a small family of undistorted cubic structures which is stable at ambient pressure and at all temperatures up to its melting point. Also the ReO_3 structure has a completely vacant A cation site of the ABO_3 perovskite structure. This empty structure is therefore expected to allow rigid rotation of the ReO_6 octahedra.[3–5]

High-pressure x-ray and neutron-diffraction measurements[6–8] established that ReO_3 undergoes a pressure-induced second-order phase transition at $P_c=5.2$ kbar at room temperature to a cubic ($Im3$) phase. The driving force of the phase transition was shown to be the softening of the M_3 phonon mode involving rigid rotation of the ReO_6 octahedra and the octahedral rotation angle was identified as an order parameter of the phase transition.[7,8] Further pressure-induced phase transitions at higher pressures have been reported.[9–11] We determined the pressure-temperature phase diagram[12] of ReO_3 in the temperature range of 2–300 K in the medium pressure range up to about 5 kbar from our neutron-diffraction investigation on a ReO_3 single crystal. The critical pressure P_c for the transition to the high-pressure phase decreases considerably at lower temperature and the high-pressure phase can be approached by cooling at ambient pressure.

The cubic perovskite structure in ReO_3 is essentially unstable due to the softening of the M_3 phonon mode involving rigid rotation of the ReO_6 octahedra. The rigid unit modes (RUMs) involved in the structural instability should lead to negative thermal expansion (NTE).[13] We therefore investigated the temperature dependence of the lattice parameter of ReO_3 by neutron diffraction.[14] We found indeed the negative thermal expansion in ReO_3 at low temperatures. The lattice parameter and the unit-cell volume decrease continuously as the temperature is increased from $T=2$ K to about $T=200$ K. After exhibiting a minimum at about 200 K they increase linearly up to about 305 K, the maximum temperature investigated. In order to understand the negative thermal expansion behavior in ReO_3 we have also carried out lattice-dynamical calculation.[14] Our calculations show that the negative thermal expansion of ReO_3 is due to the unusually large anharmonicity of the soft M_3 mode, which consists of rigid antiphase rotations of the neighboring ReO_6 octahedra. During the present investigation we determined the temperature and pressure dependences of the M_3 phonon mode by inelastic neutron scattering on a single crystal. We used our previous lattice-dynamical calculations[14] to model the temperature and pressure dependences of the M_3 phonon mode and have successfully explained qualitatively the experimental results obtained during the present study.

We have organized the paper in the following way. In Sec. II we have described the results of our inelastic neutron-scattering experiments. In Sec. III we have outlined the results of our lattice calculations and compared them with the experimental results of the inelastic neutron-scattering investigations. Finally in Sec. IV we summarized the results and made some conclusions.

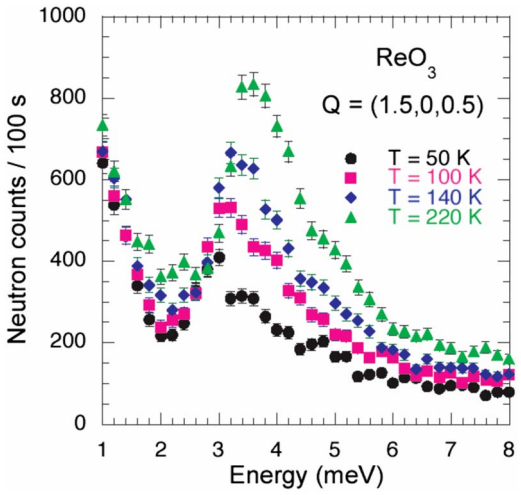

FIG. 1. (Color online) Energy scans at $Q=(1.5,0,0.5)$ in ReO_3 at several temperatures.

II. INELASTIC NEUTRON SCATTERING

We did inelastic neutron-scattering investigation on ReO_3 on the thermal triple-axis spectrometer IN8. A ReO_3 single crystal of size $4\times4\times5$ mm^3 was first put inside an Orange cryostal with its [010] crystallographic axis parallel to the $A3$ axis of the spectrometer. We used the double-focusing pyrolytic graphite PG(002) monochromator and analyzer with fully open configuration. We also used doubly focusing Si monochromator in the experiment where we studied the temperature dependence of the M_3 phonon mode. The spectrometer was used in constant k_f mode with k_f fixed to $k_f=2.662$ Å^{-1}. We first determined the temperature dependence of the M_3 phonon mode in the temperature range of 2–280 K. Figure 1 shows the constant-Q energy scans of the M_3 phonon mode at $Q=(1.5,0,0.5)$ at several temperatures. Figure 2 shows the temperature variation of the energy of the M_3 phonon mode. The energy of the M_3 phonon mode of ReO_3 decreases with decreasing temperature almost linearly. This behavior is contrary to the normal behavior of the hardening of phonon energy. The M_3 phonon softening at lower temperature is however consistent with the negative thermal expansion observed in ReO_3 by us.[14] This behavior is also expected from the pressure-temperature phase diagram of ReO_3. The high-pressure phase of ReO_3 can be approached by cooling at ambient pressure and in fact ReO_3 undergoes temperature-induced $Pm3m$-to-$Im3$ phase transition at $T_c=50$ K at $P=2.5$ kbar.

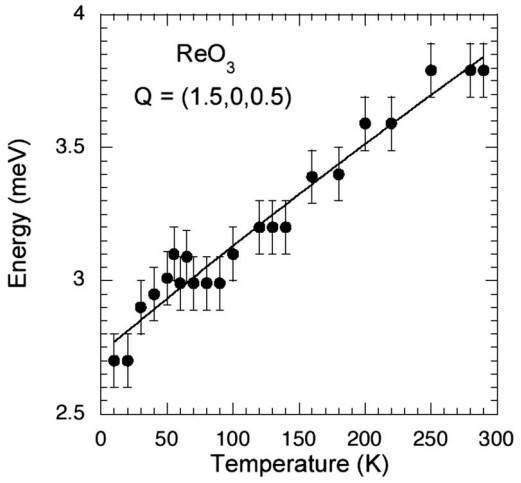

FIG. 2. Temperature dependence of the M_3 phonon mode in ReO_3. The continuous curve is a guide to the eye.

In the second part of the experiment we put the single crystal inside a gas pressure cell. The pressure cell was in turn put inside the He cryostat. We determined the pressure dependence of the M_3 phonon mode in ReO_3 at $T=150$ K. This enables one to study the high-pressure phase with the gas pressure cell that can generate pressure only up to 5 kbar. The lower temperature was chosen because the critical pressure of the transition in ReO_3 is considerably reduced at lower temperature.[12] The critical pressure at room temperature is $P_c=5.2$ kbar and that at $T=150$ K is only $P_c=3.5$ kbar that is easily accessible with the gas pressure cell. The penalty however is the loss of phonon intensity and reduction in the energy of the phonon mode making it closer to the incoherent elastic peak. We measured constant-Q energy scans of the M_3 phonon mode at several pressures. Figure 3 shows the constant-Q energy scan from ReO_3 at $Q=(1.5,0,0.5)$ at ambient pressure with the crystal inside the pressure cell and also similar scans at $P=800$ bar and 1.2 kbar. The continuous curves are the results of fitting the data with two Gaussian peaks, one elastic and the other inelastic. We notice that background is very large and is mainly from the high-pressure cell and the He inside the pressure cell. The background increases rapidly with increasing pressure because of the increase in the amount of He at higher pressures. Figure 4 shows the pressure dependence of the energy of the M_3 phonon mode in ReO_3. The energy of the M_3 phonon mode, which is about 3.4 meV at 150 K, decreases continuously and becomes zero at about 3.5 kbar. These results do not quite agree with those reported earlier by Axe *et al.*[7] The reason for this disagreement is clear from Fig. 2 of the paper.[7] Axe *et al.*[7] wrongly assigned the M_3 phonon mode to sharp peaks consisting of one or two data points at higher pressure. These peaks are too sharp to be the phonon signals and must be caused by spurious scattering events. In fact the M_3 phonon mode is broadened considerably at higher pressure as is clearly seen from our data of Fig. 3.

III. LATTICE-DYNAMICAL CALCULATIONS

We have carried out lattice-dynamics calculations with an aim to understand the apparently anomalous variation of the soft phonon frequency with change in pressure or temperature. We have observed an increase in the frequency with increasing temperature and its decrease with increasing pressure. Both these observations are opposed to the usual variation of most frequencies in most materials. Moreover, we observed the different behavior with increasing pressure or temperature when the volume decreases in both cases. As we explain below, the calculations are able to reproduce the anomalous behavior quite satisfactorily and bring out the underlying features of the interatomic potential. Temperature

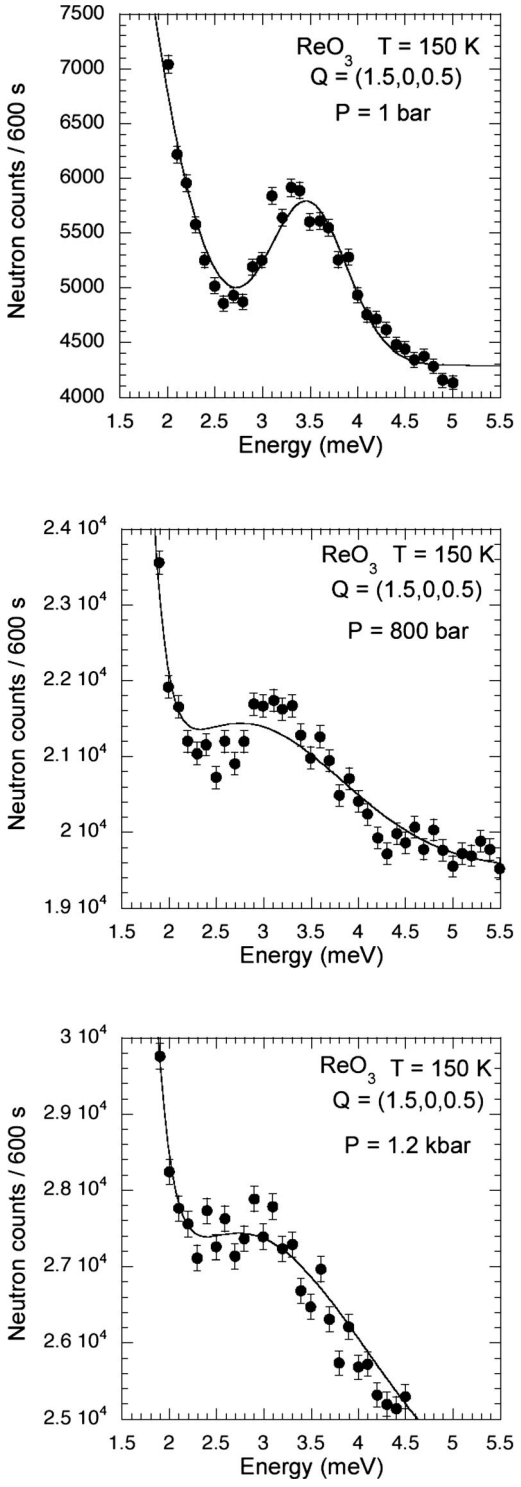

FIG. 3. Energy scans at $Q=(1.5,0,0.5)$ in ReO_3 at several pressures. The continuous curves are the results of fitting the data with two Gaussian peaks, one elastic and the other inelastic.

and pressure variations of the phonon frequency are known to occur due to anharmonicity[15–17] of the interatomic potential. There are two effects: one is the so-called *implicit* effect due to the change in volume with temperature or pressure and the other one is called the *explicit* effect due to the increase in vibration amplitude with temperature. The implicit

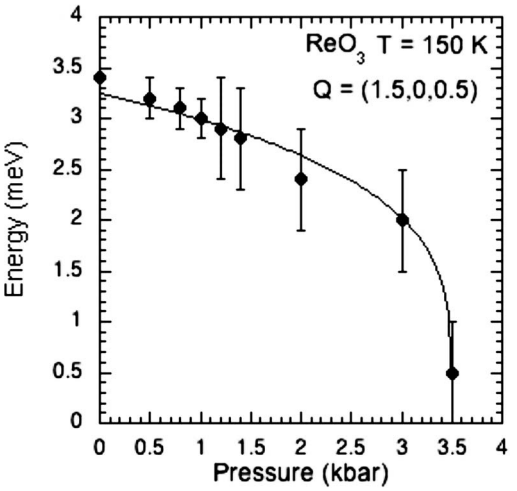

FIG. 4. Pressure dependence of the M_3 phonon mode in ReO_3. The continuous curve is a guide to the eye.

effect can be calculated in the quasiharmonic approximation, where the vibrations are assumed to be harmonic around the equilibrium positions of the atoms in a lattice of a given volume. The calculation of the explicit effect is rather complex, which in general involves phonon-phonon interactions besides self-anharmonicity. However, the latter gives a very good indication of the anharmonicity. If the anharmonicity is small, the explicit effect may be estimated by treating the anharmonic part of the potential as a perturbation. When the anharmonicity is very large, a perturbation approach is not adequate. Earlier, we carried out a classical calculation of the vibrational frequency for a given potential well.[17]

The lattice-dynamics calculations are based on the shell model that we previously reported[14] for ReO_3. A semiempirical interatomic potential is used consisting of Coulombic and short-range terms. The polarizability of the oxygen atoms has been accounted for in the framework of the shell model.[18,19] Now we have tuned the shell charge $Y(O)=-2.0$ and shell-core force constant $K(O)=74$ eV^{-2} for oxygen atoms such that at ambient pressure the calculated quasiharmonic frequency of M_3 mode is close to the experimental value. For calculations at high pressures the crystal structures are calculated at each pressure by minimization of the free energy. The calculated structures at various pressures are

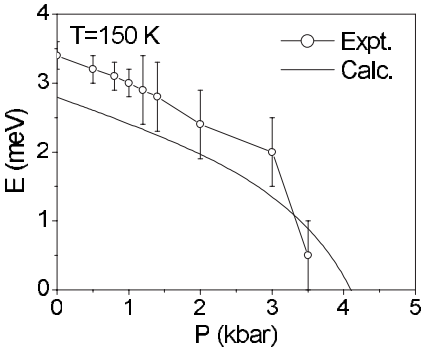

FIG. 5. Comparison of the calculated and experimental pressure dependences of M_3 mode in ReO_3.

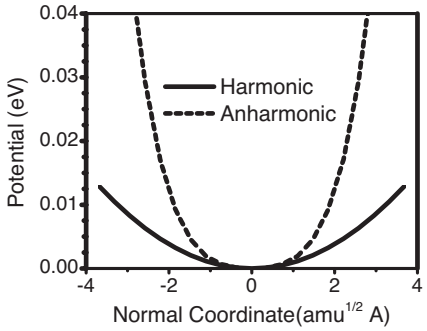

FIG. 6. The calculated potential of M_3 mode in ReO_3.

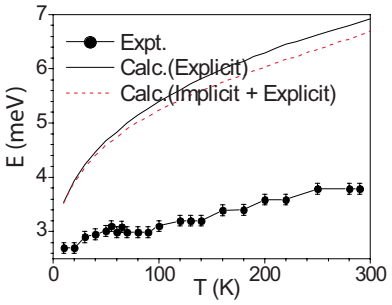

FIG. 7. (Color online) Comparison of the calculated and experimental temperature dependences of M_3 mode in ReO_3. At $T=0$ K the harmonic value of M_3 mode is 2.8 meV.

then used for the calculation of phonon frequencies at those pressures in the quasiharmonic approximation. The calculated pressure dependence of the quasiharmonic phonon frequencies for M_3 mode is in very good agreement (Fig. 5) with our experimental results. As noted above, for the temperature dependence both the implicit and explicit effects are present. The implicit effect is calculated from the known negative thermal expansion and the calculated volume dependence. Figure 5 allows estimating the implicit change in the frequency with change in volume. Since the volume decreases with temperature, the implicit change with temperature is estimated to be negative from Fig. 5.

For the calculation of explicit effect, we have first calculated the potential well of M_3 mode as shown in Fig. 6. The potential well is highly anharmonic with a large positive quadratic anharmonicity, which leads to an increase in the frequency with increase in amplitude of vibration. Since the anharmonicity is very large, we cannot use a perturbation approach to calculate the frequency changes. Hence, we resorted to a classical calculation of the vibrational frequency for the given potential well and given maximum energy according to the temperature. We have not attempted a rigorous calculation including phonon-phonon interactions. Thus the calculated explicit effect should be taken as qualitative. The comparison between the calculated and experimental temperature dependences of M_3 mode is shown in Fig. 7, where we have included both the implicit and explicit effects.

The calculation is able to reproduce the observed anomalous trends, namely, the decrease in the soft mode frequency with pressure and its increase with temperature. Both these changes involve a compression of the lattice. The former is consistent with the negative-mode Grüneisen parameters associated with the known negative thermal expansion behavior. The increase in the frequency with temperature essentially results from the positive quadratic anharmonic part of the phonon potential, which is satisfactorily brought out by the calculations. However our calculations fall short to reproduce quantitatively the pressure and temperature dependences of the M_3 phonon mode. They are particularly unsuccessful in reproducing the temperature dependence of this phonon mode. The reason is the high anharmonicity of the phonons. Also phonon-dispersion data of all the phonon modes are not available and therefore we could not derive better model parameters.

IV. SUMMARY AND CONCLUSIONS

We have investigated the temperature and pressure variations of the M_3 phonon mode of ReO_3 by inelastic neutron scattering. Contrary to the normal temperature variation of the phonon modes, the energy of the M_3 phonon mode in ReO_3 decreases with decreasing temperature. The energy of this mode also decreases with increasing pressure and tends to zero at about 3.5 kbar at $T=150$ K. The M_3 mode softening drives the pressure-induced phase transition in ReO_3. The temperature-induced softening of the M_3 mode at low temperature can be understood from the known negative thermal expansion behavior[14] and also from the fact that the high-pressure phase can also be approached at ambient pressure by cooling.[12] We have carried out lattice-dynamics calculations with an aim to understand the apparently anomalous variation of the soft phonon frequency with change in pressure or temperature. The lattice-dynamics calculations are based on the shell model that we previously reported[14] for ReO_3. A semiempirical interatomic potential is used consisting of Coulombic and short-range terms. Temperature and pressure variations of the phonon frequency are known to occur due to anharmonicity[15–17] of the interatomic potential. There are two effects: one is the so-called implicit effect due to the change in volume with temperature or pressure and the other one is called the explicit effect due to the increase in vibration amplitude with temperature. The implicit effect is calculated from the known negative thermal expansion and the calculated volume dependence. For the calculation of explicit effect, we calculated the potential well of M_3 mode. For calculations at high pressures, the crystal structures are calculated at each pressure by minimization of the free energy. The calculated structures at various pressures are then used for the calculation of phonon frequencies at those pressures in the quasiharmonic approximation. The calculation is able to reproduce the observed anomalous trends, namely, the decrease in the soft mode frequency with pressure and its increase with temperature while both the changes involve a compression of the lattice.

In conclusion we have observed anomalous temperature and pressure variation of the energy of the M_3 phonon mode in ReO_3 by inelastic neutron scattering. We have been able to reproduce these anomalous results qualitatively from our lattice-dynamics calculations based on the shell model using a semiempirical interatomic potential consisting of Coulombic and short-range terms.

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